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**IMPROVEMENT IN CYCLIC OXIDATION OF THE  
NICKEL-BASE SUPERALLOY B-1900 BY  
ADDITION OF ONE PERCENT SILICON**

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# ABSTRACT

Cast B-1900 with and without 1 weight percent Si was subjected to cyclic oxidation at 1000° and 1100° C in air for 700 and 200 hours, respectively. The results were judged by specific weight change, metallography and X-ray diffraction. Si was found to be of significant value in reducing oxidation attack, probably by increasing scale adherence.

# IMPROVEMENT IN CYCLIC OXIDATION OF THE NICKEL-BASE SUPERALLOY

## B-1900 BY ADDITION OF ONE PERCENT SILICON

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### SUMMARY

B-1900 was cast with and without a 1 weight percent addition of silicon (Si). These alloys were tested in cyclic oxidation at 1000° and 1100° C in air for 700 and 200 hours, respectively. Each cycle consisted of 6 minutes in the furnace hot zone and 9 minutes cooling. The oxidation attack was judged by metallography and specific weight change. At 1000° C unmodified B-1900 gained weight initially and then began to lose weight at an increasing rate until the termination of the test. B-1900 with 1 percent Si gained weight slightly throughout the tests at both 1000° and 1100° C. From these data and the observation of a decrease in the depletion zone thickness, Si was judged to have a marked, favorable effect on the cyclic oxidation of B-1900. The decreased spalling of the oxide on the B-1900 with 1 percent Si is likely due to increased adherence rather than a change in the oxides present as compared to unmodified B-1900 since the same oxides formed on both alloys.

### INTRODUCTION

Nickel-base superalloy turbine blades are used at high temperatures under oxidizing conditions. Exposure conditions include frequent thermal cycling, a fact that is often not taken into account in oxidation studies even though thermal cycling often results in much more severe attack than isothermal testing. The increased severity is associated with oxide spalling induced by thermal stresses. The small number of cyclic oxidation studies is evident in surveys of oxidation research (refs. 1 and 2).

Recent investigations (refs. 3 and 4) have been conducted on the effects of silicon (Si) additions on the oxidation behavior of the principal phases found in Ni-base superalloys or their coatings. These are: (1) the Ni-rich solid solution matrix phase  $\gamma$ ; (2) the ordered face-centered-cubic, precipitation-hardening phase  $\gamma'$  (basically trinickel aluminide,  $\text{Ni}_3\text{Al}$ ); and (3) the nickel-aluminide-based phase  $\beta$  in coatings. It was shown that the addition of Si markedly improves (by a factor of more than 6) the resistance of  $\gamma'$  to cyclic oxidation (ref. 4). The improvement was such that the addition of 1 percent Si resulted in a material as resistant to cyclic oxidation as unalloyed  $\beta$ . While this work (ref. 4) was conducted on simple Ni-Al compositions it indicated that Si might offer improvements in a complex commercial superalloy. Since Si was most beneficial to the oxidation resistance of  $\gamma'$  it would appear that practical utilization of this observation would be most profitable

in a commercial alloy containing a high volume fraction of  $r'$ . Thus, B-1900, a commercial alloy currently used in gas turbine engines and one that contains about 64 volume percent  $r'$  was selected for this study.

The work reported here is part of a program to determine the effects of Si on the oxidation and mechanical behavior of B-1900 as a function of Si concentration. Some Si is present in all cast nickel-base superalloys but it is not typically added intentionally and is generally limited to a maximum of 0.2 to 0.5 weight percent. The reasons for setting these maximum concentrations are not clear in superalloy literature. So, it seemed reasonable to conduct a study to learn if higher Si concentrations can improve oxidation resistance without degrading mechanical properties.

The present work is an initial study to determine if Si is effective in reducing the attack of cyclic oxidation on B-1900. The temperatures chosen were 1000° and 1100° C. In order to get substantial oxidation attack, high frequency cycling, consisting of 6 minutes in the furnace and 9 minutes cooling, was used. Even then, long times were required for substantial attack: 700 hours at 1000° C and 200 hours at 1100° C. Samples were evaluated by weight change. Microstructural and X-ray diffraction analyses were also made.

## MATERIALS AND PROCEDURES

### Materials

Two slabs of B-1900 approximately 7.6 by 7.6 by 1.2 centimeters were cast under vacuum from a single master heat. To one casting 1 weight percent silicon was added during remelting. The master alloy was purchased from a commercial supplier of B-1900. Coupons for oxidation testing 1.2 by 1.9 by 0.2 centimeters were cut from both castings and surface ground on all sides. They were rinsed in methanol before testing.

The compositions of the master alloy and the two castings were determined by a commercial laboratory using wet chemical analysis techniques and are shown in table I. There is less than a 2 percent variation in the compositions except for the zirconium concentration which is up from 0.05 percent in the master alloy to 0.2 to 0.3 in the castings and, of course, the silicon concentration which was 0.99 percent in the alloy to which it was added.

The microstructures of the two alloys in the as-cast condition are shown in figure 1. They have essentially the same microstructure typical of cast nickel-base superalloys. The minor phases in both alloys were identified by X-ray diffraction studies of electrolytically extracted residues. The minor phases were extracted using an electrolyte of 10 percent HCl in methanol and a current density of about 100 milliamperes per square centimeter. An MC-type carbide and an  $M_3B_2$  type boride were

found in both alloys. In addition, the B-1900 plus Si alloy was found to contain a face-centered cubic phase with a lattice parameter of 3.46 angstroms tentatively identified as  $\text{Ni}_3\text{Si}$ . This phase was not, however, evident in the microstructure of this alloy when using light microscopy.

### Oxidation

The apparatus used in this investigation for thermal cycling in static air is shown in figure 2. It can be automatically actuated for a wide variety of heating and cooling times. When the sample is raised from the furnace, it is surrounded by a water cooled baffle under which is a spall collector. At intervals the sample is weighed and the spall analyzed. In this program the samples were kept in the furnace for 6 minutes and raised for 9 minutes. This constituted one cycle.

The thermal lag of the samples was such that upon insertion into the furnace, the samples reached temperature in about 1 minute. Upon removal, the samples cooled below  $500^\circ\text{C}$  in about 1 minute. The duration of the tests were 7000 cycles (700 hr exposure) at  $1000^\circ\text{C}$  and 2000 cycles (200 hr exposure) at  $1100^\circ\text{C}$ .

After test, the samples and spalls were analyzed by X-ray diffraction. Adherent oxides were analyzed in situ on a diffractometer, while the spalls were run in a Debye-Scherrer powder camera. The samples were then mounted in epoxy, sectioned and examined metallographically.

### RESULTS AND DISCUSSION

The cyclic oxidation behavior of B-1900 with and without Si was judged by weight change, scale identification, and microstructural changes. These results and interpretation are presented here.

The weight change data are shown for  $1000^\circ\text{C}$  and  $1100^\circ\text{C}$  in figures 3 and 4, respectively. At both temperatures, unmodified B-1900 gains weight for many hours, about 400 hours at  $1000^\circ\text{C}$  and about 90 hours at  $1100^\circ\text{C}$ . This is followed by a gradual loss of weight until the net weight change is zero after approximately 470 hours at  $1000^\circ\text{C}$  and 96 hours at  $1100^\circ\text{C}$ . Thereafter, the loss is increasingly more rapid to the end of the test, 700 hours at  $1000^\circ\text{C}$  and 200 hours at  $1100^\circ\text{C}$ . In contrast the B-1900 with 1 weight percent Si gains weight gradually throughout the test. Furthermore, during cyclic oxidation, unmodified B-1900 showed marked spallation as the samples began to lose weight but the cyclic oxidation of B-1900 with 1 percent Si produced very slight spallation.

X-ray diffraction analyses made at the conclusion of the tests failed to reveal any differences in oxides formed. The X-ray patterns were mixtures of  $\text{NiO}$ , a spinel with  $a_0 = 8.21\text{\AA}$  (probably  $\text{Ni}(\text{Cr},\text{Al})_2\text{O}_4$ ), a spinel with  $a_0 = 8.08\text{\AA}$  (probably  $\text{NiAl}_2\text{O}_4$ ), a tapiolite (basically

NiTa<sub>2</sub>O<sub>6</sub> with other refractory metals substituting for Ta), and Al<sub>2</sub>O<sub>3</sub>. No Si bearing oxide was observed. The spalls and in situ oxides gave similar patterns. In general the NiO pattern seemed stronger in the unmodified B-1900, while Al<sub>2</sub>O<sub>3</sub> seemed stronger in the B-1900 plus 1 percent Si. However, this difference was not pronounced. These results suggest that the difference in spallation is not due primarily to what oxides form but is more likely due to their adherence qualities.

The microstructures of unmodified B-1900 and B-1900 with 1 percent Si after 200 hours of cycling at 1100° C are shown in figure 5. The 1000° C microstructures (not shown) were similar. The depletion zone typical of oxidized nickel-base superalloys is apparent. These are formed by surface depletion of Al reducing the composition below the Al level needed for  $\gamma'$  formation. Note the depletion zone of B-1900 is approximately 60  $\mu$ m while that of B-1900 plus 1 percent Si is about 15  $\mu$ m. Two other features are worth noting. The first is that the oxide-metal interface of the Si-containing alloy is smoother than that of the unmodified alloy. This is probably a result of the more extensive attack on the unmodified alloy, but it raises an interesting point. It has often been said that the presence of a smooth oxide-metal interface is prone to spallation. Conversely, a jagged interface is said to retard spallation. Neither observation appears to apply here. The second feature to note is that the oxide covering the B-1900 with 1 percent Si added is thin and adherent while that over the unmodified B-1900 is thick and loosely bound. This is what one would anticipate from lightly and grossly spalling alloys, respectively.

Increased scale adherence is thought to be the primary reason for the improvement in oxidation resistance of B-1900 with 1 percent Si added. Another possible explanation, such as a decreased rate of diffusion through the scale, must be discounted since the initial rate of weight gain was nearly the same in both the alloys investigated.

#### SUMMARY OF RESULTS

Unmodified B-1900 and B-1900 containing 1 weight percent Si were cyclically oxidized at 1000° and 1100° C for 700 and 200 hours, respectively. Each cycle consisted of 6 minutes in the furnace followed by 9 minutes of cooling. Specific weight change, X-ray diffraction, and metallographic data were obtained. The major results of this work are as follows:

1. At both 1000° and 1100° C, the B-1900 with 1 percent Si had superior cyclic oxidation resistance to unmodified B-1900 as judged by weight change and spallation.

2. The microstructure of B-1900 with 1 percent Si showed a smoother metal-scale interface and smaller depletion zone than unmodified B-1900.

3. X-ray diffraction of in situ scales and spalled oxides showed no appreciable differences between the scales formed on the two alloys.

#### CONCLUDING REMARKS

Based on specific weight change and spall evaluation as well as supplementary metallographic analyses, the addition of 1 percent Si to B-1900 markedly improves the resistance of the alloy to cyclic oxidation. Specifically, the Si reduces the tendency toward oxide spallation thereby preventing rapid oxidation and increased weight loss.

The mechanism of the improvement remains obscure and is being investigated. Since the oxide phases formed, as determined by X-ray diffraction, were the same for the two alloys, there are no obvious clues as to the mechanism involved. The effects are apparently quite subtle and will require further study.

Before the beneficial effects of Si on oxidation resistance can be fully exploited it will be necessary to determine its effect as a function of concentration on both oxidation resistance and mechanical properties. If the 1 percent Si level studied in this work greatly impairs the mechanical properties of B-1900, other silicon concentrations should be considered from the dual standpoint of their effect upon oxidation resistance and mechanical properties. Also, the addition of Si to the surface of B-1900 as part of a coating cycle might be investigated. Finally, it must be emphasized that the beneficial effect of Si on cyclic oxidation needs to be confirmed in a high-velocity gas stream.

#### REFERENCES

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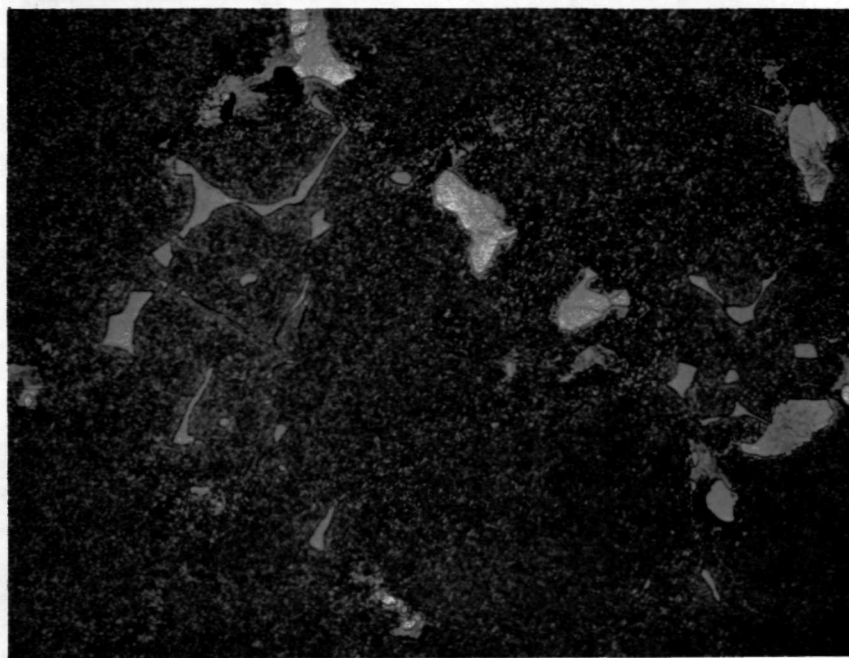


TABLE I. - CHEMICAL ANALYSES<sup>a</sup>

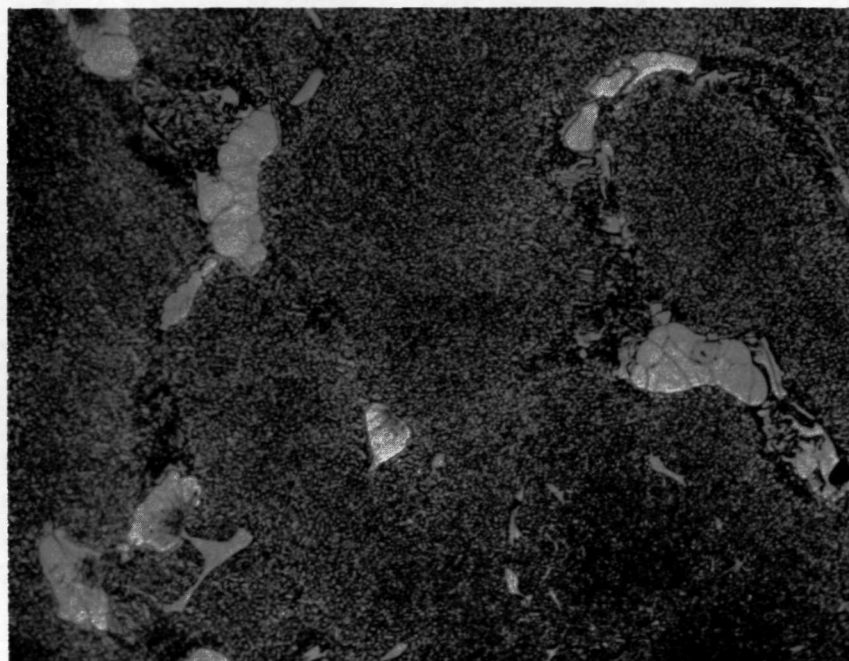
All values are in weight percent.

	Master B-1900	Re-cast B-1900	Re-cast B-1900+Si
Chromium	7.97	7.93	7.76
Aluminum	6.28	6.08	5.98
Cobalt	10.17	10.14	10.08
Molybdenum	6.33	6.35	6.25
Tantalum	4.48	4.48	4.41
Titanium	1.09	1.12	1.10
Zirconium	.05	.21	.34
Silicon	.03	.06	.99
Carbon	.001	.001	.001
Boron	.014	(b)	(b)
Nickel	Balance	Balance	Balance

<sup>a</sup>Net analysis by a commercial laboratory.<sup>b</sup>Not analyzed.



(a) As-cast B-1900.



(b) As-cast B-1900 + Si.

Figure 1. - Effect of one weight percent Si on microstructures of re-cast B-1900. Etched with 33 water, 33 nitric acid, 33 acetic acid, and 1 hydrofluoric acid. X250.

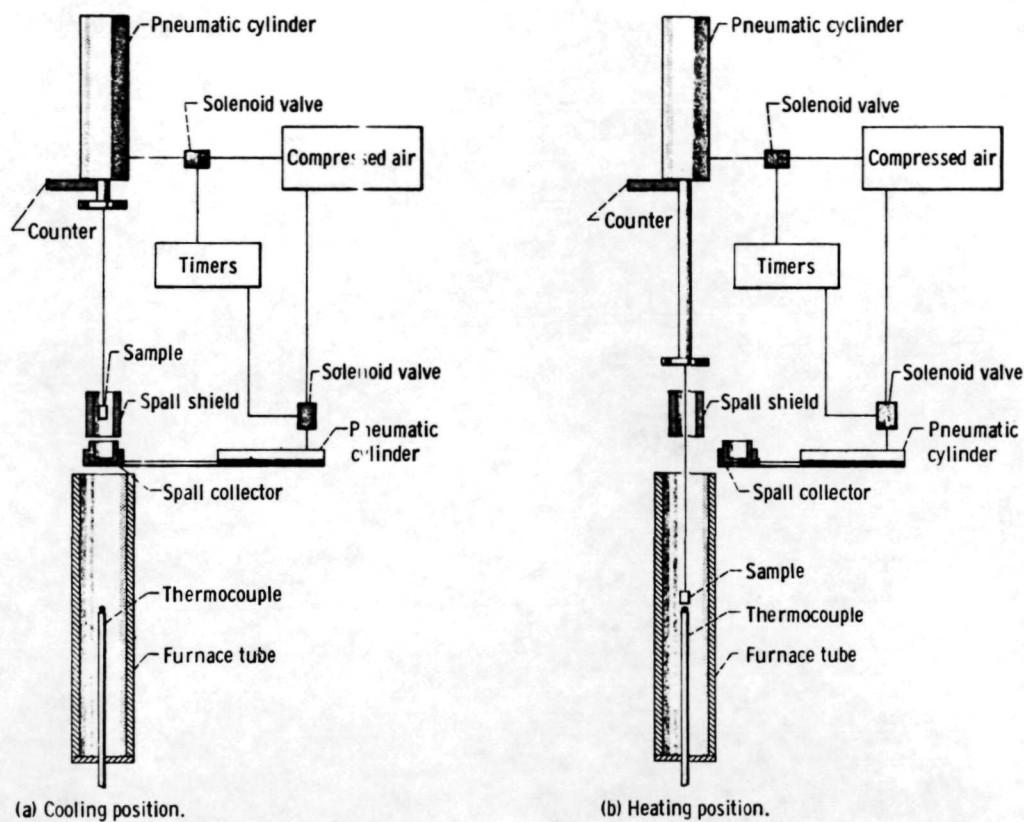


Figure 2.- Automatic cycling and spall collecting apparatus.

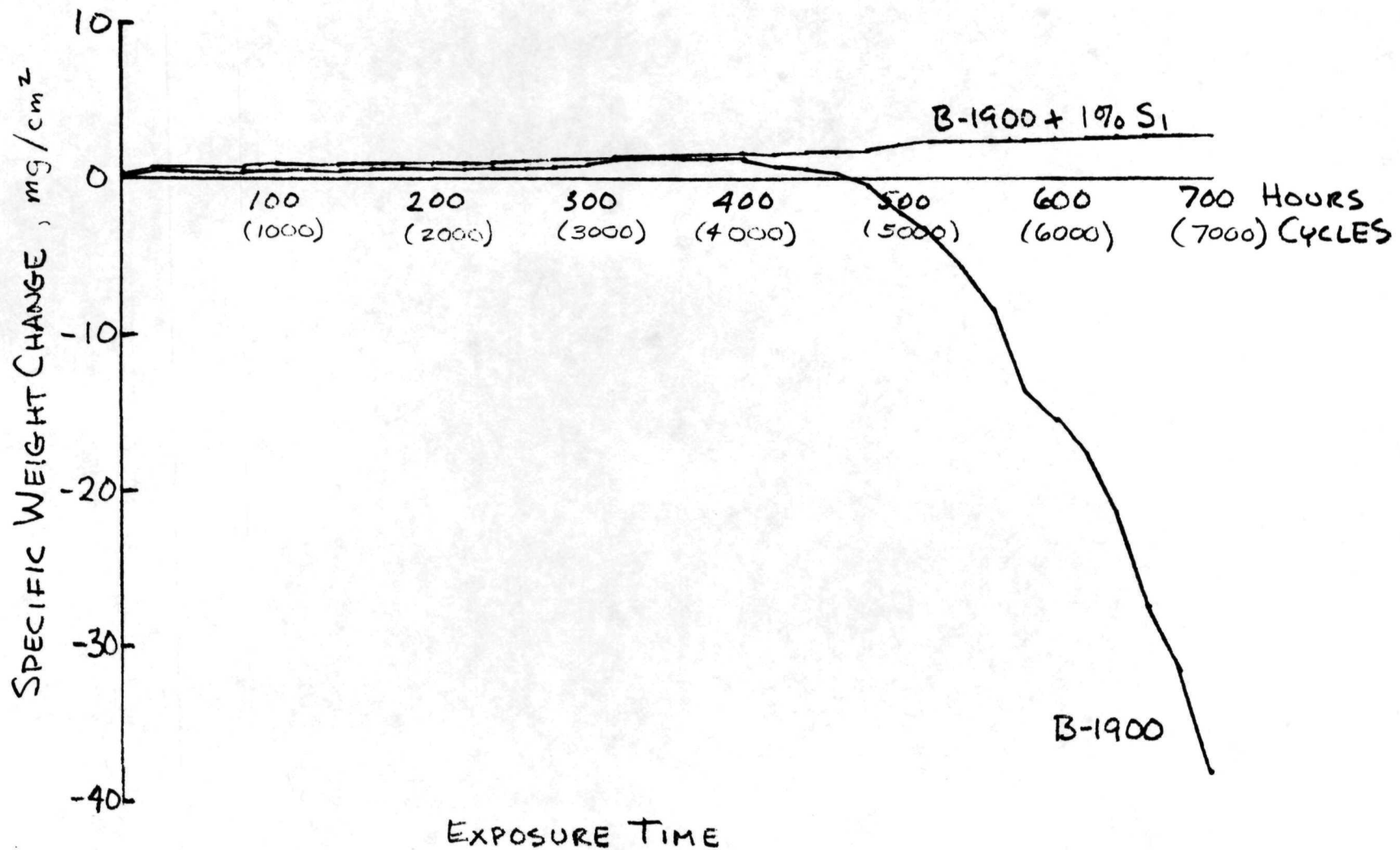


FIGURE 3. THE EFFECT OF Si ON THE RESISTANCE TO CYCLIC OXIDATION <sup>OF B-1900</sup> AT 1000°C. Cycle consists of 6 minutes in the furnace and 9 minutes cooling.

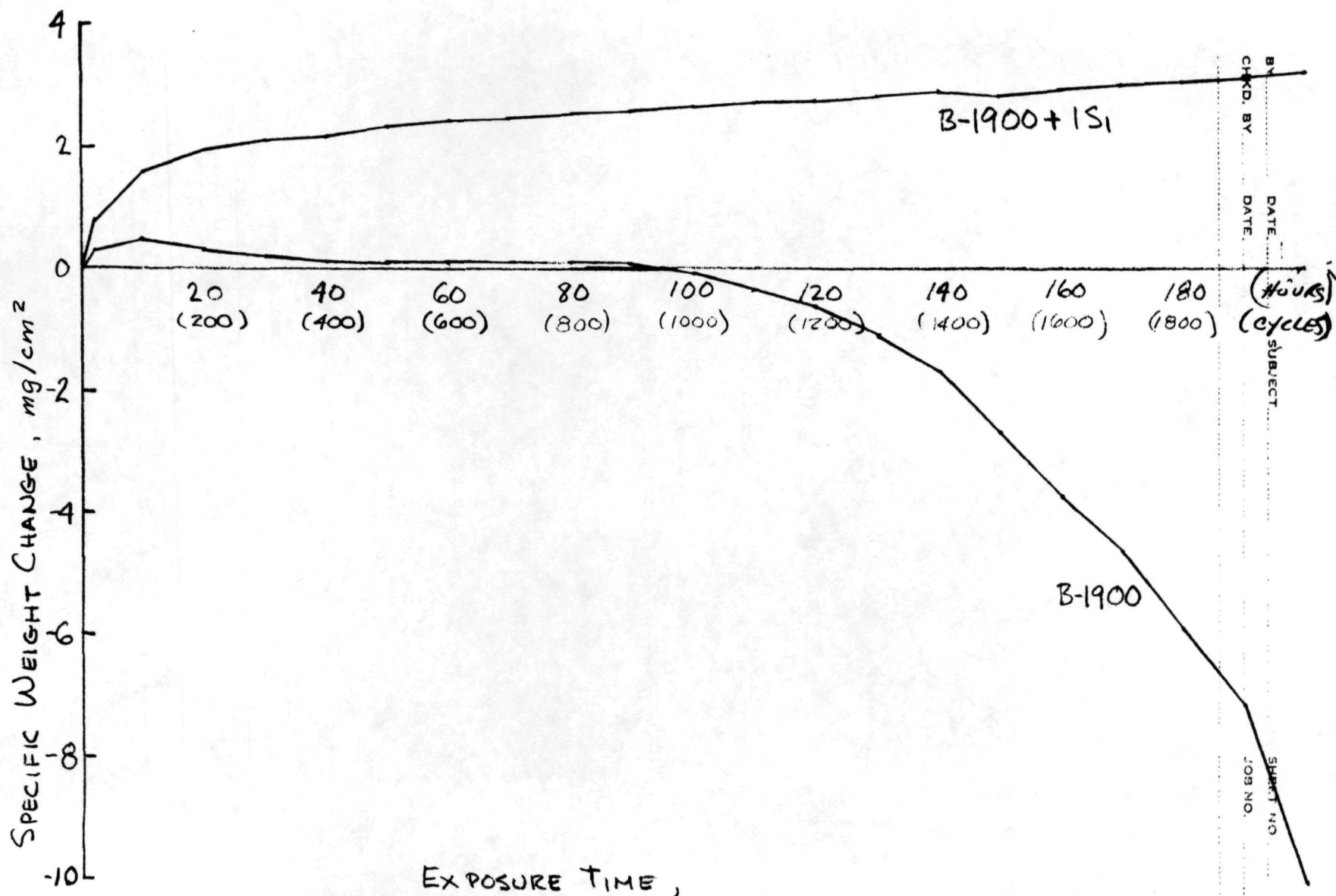
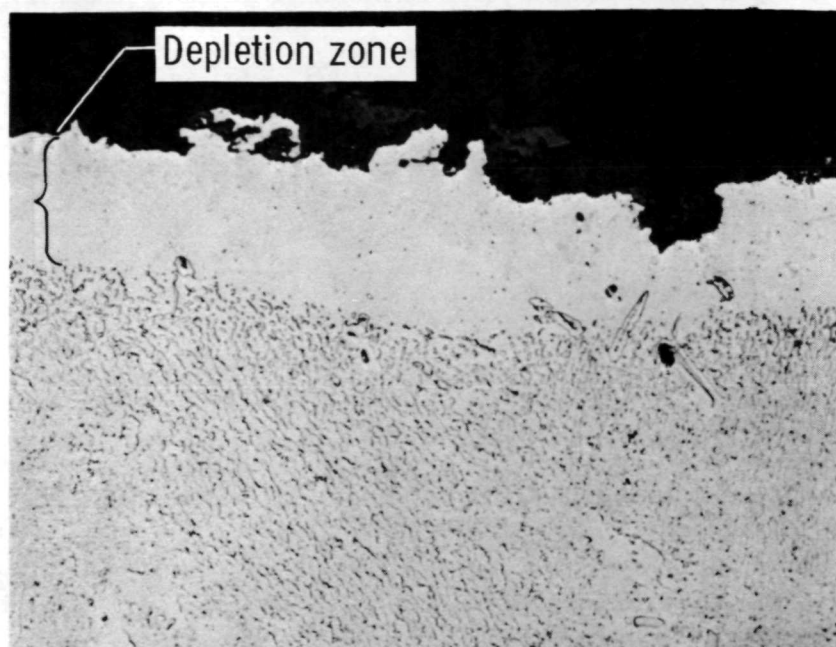
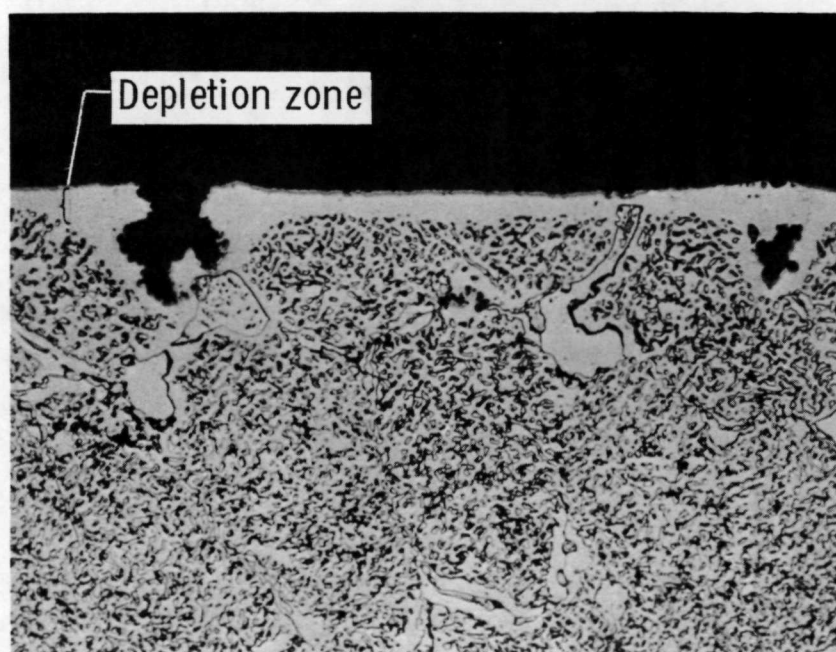


FIGURE 4. THE EFFECT OF Si ON THE CYCLIC OXIDATION RESISTANCE OF B-1900 AT  $1100^\circ\text{C}$ . cycle consists of 6 minutes in the furnace and 9 minutes cooling.



(a) B-1900.



(b) B-1900 + 1 Si.

Figure 5. - Microstructural effects of Si on thermal cycling of B-1900 during oxidation at  $1100^{\circ}\text{C}$ . 2000 cycles (200 hours at temperature). Etched with 33 acetic acid, 33 nitric acid, 33 water, and 1 hydrofluoric acid. X250.